Mark Buscheck • Charles Noyes

Lawrence Livermore National Laboratory (LLNL) samples and analyzes groundwater from areas of known or suspected contamination. Portions of the two sites where soil or groundwater contain or may contain chemicals of concern are actively investigated to define the hydrogeology, nature, and extent of the contamination and its source. Where necessary, remediation strategies are developed and evaluated through preparation of a Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) removal action or through the CERCLA feasibility study process. An approved remedy for each area is developed in consultation with the regulatory agencies and the community.

This chapter reviews the distribution of contaminants in groundwater and the progress LLNL has made in removing contaminants from groundwater and from the unsaturated zone (soil vapor) at the Livermore Site and Site 300. The sites are similar in that the contamination is, for the most part, confined on-site. The sites differ in that Site 300, with an area of 28.3 km² (10.9 mi²), is much larger than the Livermore Site and has been divided into nine Operable Units (OUs) based on the nature and extent of contamination, and topographic and hydrologic considerations. The Livermore Site, at 3.3 km² (1.3 mi²), is effectively one OU.

7.1 Livermore Site Environmental Restoration Project

Initial releases of hazardous materials occurred at the Livermore Site in the mid-to-late 1940s during operations at the Livermore Naval Air Station (Thorpe et al. 1990). There is also evidence that localized spills, leaking tanks and impoundments, and landfills contributed volatile organic compounds (VOCs), fuel hydrocarbons, metals, and tritium to the unsaturated zone and groundwater in the post-Navy era. The Livermore Site was placed on the U.S. Environmental Protection Agency (EPA) National Priorities List in 1987.

An analysis of all environmental media showed that groundwater and both saturated and unsaturated soils are the only media that require remediation (Thorpe et al. 1990). Compounds that currently exist in groundwater at various locations beneath the site at concentrations above drinking water standards (maximum contaminant levels [MCLs]) are trichloroethylene (TCE), tetrachloroethene (PCE), 1,1-dichloroethylene, cis-1,2-dichloroethylene, 1,1-dichloroethane, 1,2-dichloroethane, carbon tetrachloride, vinyl chloride, and tritium. PCE is also present at low concentrations slightly above the MCL in an off-site groundwater plume that extends from the southwestern corner of the Livermore Site. LLNL operates groundwater extraction wells in both on-site and off-site areas. In addition, LLNL maintains an extensive network of groundwater monitoring wells in the off-site area west of Vasco Road.

7.1.1 Physiographic Setting

The general topography of the Livermore Site is described in **Chapter 1**. The Livermore Valley groundwater system consists of several semiconfined aquifers. Rainfall from the surrounding hills

and seasonal surface water in the arroyos recharge the groundwater system, which flows toward the east-west axis of the valley.

The thickest sediments and aquifers are present in the central and western portions of the Livermore Valley, where they form an important resource for the Zone 7 Water Agency. These sediments comprise two aquifers: the Livermore Formation and overlying alluvium. The Livermore Formation averages about 1,000 m in thickness and occupies an area of approximately 250 km². The alluvium, which is about 100 m thick, is the principal water-producing aquifer within the valley.

7.1.2 Hydrogeology of the Livermore Site

Sediments at the Livermore Site are grouped into four grain-size categories: clay, silt, sand, and gravel. Groundwater flow beneath the site occurs primarily in alluvial sand and gravel deposits, which are bounded by lower permeability clay and silt deposits. The alluvial sediments have been subdivided into nine hydrostratigraphic units (HSUs) beneath the Livermore Site. HSUs are defined as sedimentary sequences whose permeable layers show evidence of being hydraulically interconnected and geochemically similar. Six of the nine HSUs contain contaminants at concentrations above their MCLs: HSU-1B, -2, -3A, -3B, -4, and -5 (Blake et al. 1995; Hoffman et al. 2003). HSU-1A, -6, and -7 do not contain contaminants of concern above action levels.

7.1.3 Remediation Activities and Monitoring Results

In 2021, LLNL operated and/or maintained 27 groundwater treatment facilities (TFs). The groundwater extraction wells and dual (groundwater and soil vapor) extraction wells produced 961 million L of groundwater and the TFs removed about 26 kg of VOCs. Since remediation began in 1989, approximately 26.54 billion L of groundwater have been treated, resulting in removal of more than 1,825 kg of VOCs. Additional information concerning flow and mass removal by treatment facility area is presented in Noyes et al. (2022).

LLNL also operated and/or maintained eight soil vapor treatment facilities (VTFs) in 2021. The soil vapor extraction wells and dual extraction wells produced more than 3.9 million m³ of soil vapor and the treatment facilities removed approximately 12 kg of VOCs. Since initial operation, nearly 36.5 million m³ of soil vapor have been extracted and treated, removing more than 1,642 kg of VOCs from the subsurface. Additional information concerning flow and mass removal by treatment facility area is presented in Noyes et al. (2022).

Five treatment facilities remained offline in 2021:

- Vapor Treatment Facility D (VTFD) Helipad
- TF5475-1
- TF5475-3
- VTF5475
- TF518 North

VTFD¹ Helipad remained offline in support of the *in situ* bioremediation Enhanced Source Area Remediation (ESAR) treatability test at the TFD Helipad Source area. The four remaining facilities were discussed in LLNL (2009). With the U.S. EPA concurrence, restart of these four facilities has been deferred pending the results of ESAR treatability tests. LLNL continues to monitor groundwater for VOCs and tritium. See Noyes et al. (2022) for more information on the Livermore Site groundwater and soil VTFs.

Restoration activities in 2021 at the Livermore Site continued to be primarily focused on enhancing and optimizing ongoing operations at TFs, while continuing to evaluate technologies that could be used to accelerate cleanup of the Livermore Site source areas and to address the mixed-waste management issue discussed in the *Draft Focused Feasibility Study of Methods to Minimize Mixed Hazardous and Low Level Radioactive Waste from Soil Vapor and Ground Water Treatment Facilities at the Lawrence Livermore National Laboratory Site* (Bourne et al. 2010).

In 2021, the ESAR treatability tests continued at TFD Helipad (*in situ* bioremediation), TFE Eastern Landing Mat (thermally-enhanced remediation), and TFC Hotspot (emplacement of zero valent iron [ZVI] for *in situ* VOC destruction).

Additional Livermore Site environmental restoration activities performed in 2021 included:

- Conducting a Cone Penetrometer Testing (CPT) and direct-push drilling soil vapor and soil sampling survey for VOCs in the TFD area.
- Drilling and installing four new monitoring wells in the TFD area.
- Drilling and sampling four performance-monitoring boreholes at the TFD Helipad and TFC Hotspot ESAR treatability tests.
- Continued enhancement and optimization of ongoing operations at TFs across the site.
- Continued reevaluation of the inhalation risk for VOCs potentially migrating from the subsurface into indoor ambient air, including sampling of a prioritized list of buildings. In 2021, the EPA determined that the current remedy is protective in the short-term.

Groundwater concentration and hydraulic data indicate subtle but consistent declines in the VOC concentrations and areal extent of the contaminant plumes in 2021. Hydraulic containment along the western and southern boundaries of the site was fully maintained in 2021, and progress was made toward interior plume and source area clean up. See Noyes et al. (2022) for the status of cleanup progress.

7.1.4 Environmental Impacts

LLNL strives to reduce risks arising from chemicals released to the environment, to conduct all its restoration activities to protect environmental resources, and to preserve the health and safety of all site workers. LLNL's environmental restoration project is committed to preventing present and future human exposure to contaminated soil, soil vapor, and groundwater, preventing further contaminant migration of concentrations above drinking water standards, reducing concentrations

¹ VTFD Helipad stands for vapor treatment facility D Helipad, a soil vapor extraction facility. TFD Helipad stands for treatment facility D which is a groundwater treatment facility. They are different and distinct facilities.

of contaminants in groundwater and soil vapor, and minimizing contaminant migration from the unsaturated zone to the underlying groundwater.

Remedial solutions that have been determined to be most appropriate for individual areas of contamination are implemented. The selected remedial solutions, which include groundwater and soil vapor extraction and treatment, have been agreed upon by the Department of Energy (DOE) and the regulatory agencies with public input. These solutions are designed to achieve the goals of reducing risks to human health and the environment and satisfying remediation objectives, and of meeting regulatory standards for chemicals in water and soil, and other state and federal requirements.

7.2 Site 300 Environmental Restoration Project

A number of contaminants were released to the environment during past LLNL Site 300 operations including waste fluid disposal to dry wells, surface spills, piping leaks, burial of debris in unlined pits and landfills, detonations at firing tables, and discharge of rinse water to unlined lagoons. Environmental investigations at Site 300 began in 1981. As a result of these investigations, VOCs, high explosive compounds, tritium, depleted uranium, organosilicate oil, nitrate, perchlorate, polychlorinated biphenyls, dioxins, furans, and metals were identified as contaminants of concern in soil, rock, groundwater, or surface water. This contamination is confined within the site boundaries with the exception of VOCs that are present in off-site monitoring wells near the southern site boundary. LLNL maintains an extensive network of onsite and off-site wells to monitor this contamination. As stated in the introduction to this chapter, all characterized contaminant release sites that have a CERCLA pathway have been assigned to one of nine OUs based on the nature, extent, and sources of contamination, and topographic and hydrologic considerations. Site 300 was placed on the EPA National Priorities List in 1990. Cleanup activities began at Site 300 in 1982 and are ongoing.

Background information for LLNL environmental characterization and restoration activities at Site 300 can be found in Webster-Scholten (1994), *Final Remedial Investigation/Feasibility Study for the Pit 7 Complex at Lawrence Livermore National Laboratory Site 300* (Taffet et al. 2005), and the *Site-Wide Remediation Evaluation Summary Report for Lawrence Livermore National Laboratory Site 300* (Ferry et al. 2006).

7.2.1 Physiographic Setting and Geology of Site 300

Site 300 is located in the southeastern Altamont Hills of the Diablo Range. The topography of Site 300 consists of a series of steep hills and canyons generally oriented northwest to southeast. The site is underlain by gently dipping sedimentary bedrock dissected by steep ravines. The near-surface bedrock consists primarily of interbedded conglomerates, sandstones, siltstones, and claystones of the late Miocene Neroly Formation (Tn), and a Pliocene nonmarine unit (Tps). Late Miocene sandstone-dominated strata of the Cierbo Formation (Tmss) locally exist in the shallow subsurface. The bedrock units are locally overlain by mid- to late-Pleistocene terrace deposits and late-Pleistocene to Holocene floodplain, ravine fill, landslide, and colluvial deposits.

The bedrock within Site 300 has been slightly deformed into several gentle, low-amplitude folds. The locations and characteristics of these folds, in combination with the regional fault and fracture patterns, locally influence groundwater flow within the site.

7.2.2 Contaminant Hydrogeology of Site 300

Site 300 is a large and hydrogeologically diverse site. Due to the steep topography and structural complexity, stratigraphic units and groundwater contained within many of these units are discontinuous across the site. Consequently, site-specific hydrogeologic conditions govern the occurrence and flow of groundwater and the fate and transport of contaminants beneath each OU.

An HSU is a laterally-extensive water-bearing zone that occurs in discrete stratigraphic units and exhibits similar hydraulic and geochemical properties. At Site 300, HSUs have been defined consisting of one or more stratigraphic intervals that compose a single hydraulic system within one or more OUs. At Site 300, groundwater movement and contaminant migration in groundwater are discussed in the context of HSUs.

Groundwater contamination at Site 300 occurs primarily in three types of HSUs:

- 1. Mixed Quaternary alluvium, terrace deposits, and landslide deposits and underlying coherent and weathered bedrock HSUs including alluvium and weathered bedrock (Qal/WBR HSU), alluvium and sandstone (Qal-Tnbs₁ HSU), terrace deposits and sandstone (Qt-Tnbs₁ HSUs), terrace deposits and claystone (Qt-Tnsc₁ HSU), and landslide deposits and sandstone (Qls/Tnbs₁ HSU). [Note: Tn refers to Tertiary Neroly Formation bedrock].
- 2. Perched groundwater in fluvial sands and gravels (Tpsg HSU), semi-lithified silts and clay of the Tpsg-Tps HSU, and silts and clay and underlying silty claystone (Tps-Tnsc₂ HSU). [Note: Tp refers to Tertiary Pliocene sediments].
- 3. Bedrock including the Tnbs₂, Tnsc_{1ab}, Tnsc_{1b}, Tnbs₁, Tnbs₁/Tnbs₀, and Tnbs₁/Tnsc₀ HSUs.

Groundwater in bedrock is typically present under confined conditions in the southern part of the site but is often unconfined elsewhere. Recharge occurs where saturated alluvial valley fill is in contact with underlying permeable bedrock, and where bedrock strata crop out. Water levels within Site 300 shallow water-bearing zones have generally been declining due to groundwater pumping and limited recharge owing to the recent California drought. During 2021, water levels in shallow water-bearing zones throughout Site 300 generally declined slightly because of the less than average 2020-2021 rainfall totals.

7.2.3 Remediation Activities and Monitoring Results

Cleanup activities were initiated at Site 300 in 1982 and are underway, have been completed, or are in the process of being implemented at the nine OUs. These activities include:

- Operating 21 groundwater and soil vapor extraction and treatment facilities.
- Capping and closing four landfills, six high explosives rinse water lagoons, and one high explosives burn pit.

- Removal and/or closure of numerous dry wells throughout the site.
- Removal of contaminated soil from source areas throughout the site.
- Installation of a drainage diversion system at the Pit 7 Complex to prevent groundwater from rising into the landfills and releasing contaminants in the waste.
- Remediation (consolidation and solidification) of 29,000 cubic yards of polychlorinated biphenyl (PCB)-, dioxin-, and furan-contaminated soil in a Corrective Action Management Unit (CAMU) at Building 850.
- Treatability studies for the *in situ* bioremediation of VOCs and perchlorate in groundwater.
- Installation and sampling of over 700 groundwater monitoring wells to track plume migration and remediation progress.

These remediation efforts have resulted in (1) the elimination of risk to on-site workers from contaminant exposure at multiple locations throughout Site 300, (2) a reduction in maximum concentrations of the primary contaminant (VOCs) in Site 300 groundwater by 50% to 99%, (3) the remediation of VOCs in groundwater in the Eastern General Services Area to meet cleanup standards, and (4) a reduction of maximum tritium activities in groundwater emanating from the Building 850 area to below cleanup standards.

In 2021, the Site 300 Environmental Restoration Project operated 12 groundwater facilities, 4 groundwater collection systems, and 5 soil vapor treatment or extraction-only facilities extracting and treating approximately 26.3 million L of groundwater and 2.2 million m³ of contaminated soil vapor. The Site 300 TFs removed about 7.7 kg of VOCs, 0.057 kg of perchlorate, 1,156 kg of nitrate, 0.084 kg of the high explosive compound RDX, and 0.003 kg of uranium in 2021. Since groundwater remediation began in 1990, approximately 1,812 million L of groundwater and 40 million m³ soil vapor have been treated, resulting in removal of approximately 642 kg of VOCs, 1.9 kg of perchlorate, 23,000 kg of nitrate, 3.0 kg of RDX, 9.5 kg of silicone oils, and 0.1 kg of uranium. Tritium in groundwater continues to decay on-site, reducing tritium activities in Site 300 groundwater. Detailed groundwater volume and contaminant mass removal totals, by OU, are presented in Buscheck et al. (2022).

To date, cleanup remedies have been fully implemented and are operational in eight of the nine OUs at Site 300 (the General Services Area, Building 834, Pit 6 Landfill, High Explosives Process Area, Building 850/Pit 7 Complex, Building 854, Building 832 Canyon OUs, and OU 8, which is comprised of four site-wide subareas). The CERCLA pathway for the last OU, Building 812, was negotiated with the regulatory agencies in 2011. At Building 812, characterization activities were initiated in 2011 and have continued in subsequent years. These activities include:

- Sampling surface soil, groundwater, and surface water for chemical and radiological analyses.
- Sampling plants and invertebrates for uranium analysis.

- Drilling and hand augering additional boreholes, collecting samples for chemical and radiological analysis, and conducting High Purity Germanium (HPGe) detector gamma radiation surveying for uranium-238 in subsurface soil to better determine its vertical extent.
- Gamma radiation surveying with a sodium iodide (NaI) detector to better define the extent of uranium-238 in Building 812 surface soil.
- Surface water discharge and velocity monitoring.
- Analyzing the chemical and radiological data collected to determine the nature and extent of contamination.

The results of characterization activities in the Building 812 OU are being analyzed and will be presented in a Remedial Investigation/Feasibility Study (RI/FS) report once updated background concentration and activity ranges for metals and radionuclides in Site 300 soil are determined and documented in a final report. Sampling and analysis of soil from nearby Mount (Mt.) Diablo State Park was completed in 2021 to provide additional analytical data for calculating updated background concentrations and activities of metals and radionuclides. Mt. Diablo State Park was selected for the soil sampling because it has similar geology, soil types, and ecology to Site 300.

Additional Site 300 Environmental Restoration Project activities performed in 2021 included:

- Installing three new groundwater monitoring wells in the Building 850 area.
- Installing one new groundwater monitoring well in the Building 834 Area.
- Installing one new groundwater monitoring well in the Building 865 area.
- Installing one new groundwater monitoring well in the Building 812 area.
- Closing three former groundwater monitoring wells in the Building 850 Area.
- Inspecting and maintaining the Pit 7 Drainage Diversion System and Building 850 Corrective Action Management Unit.
- Continuing the Building 850 In Situ Perchlorate Bioremediation Treatability Test.
- Continuing evaluation of subsurface VOC and hydrologic data to determine a next phase of treatment in the T2 area of Building 834.
- Completed upgrades to the Building 832 source area groundwater and soil VTFs.
- Completed upgrades to the Building 817 source area groundwater extraction facility.
- Continued reevaluation of the inhalation risk to workers from VOCs potentially migrating from the subsurface into indoor ambient air. In 2021, the EPA determined that the current remedies for areas with potential VOC indoor air inhalation risk continue to be protective in the short-term.

All calendar year 2021 Site 300 milestones were met or renegotiated with the regulatory agencies (see **Chapter 2**).

Groundwater concentration, activity, and hydraulic data collected and analyzed for Site 300 during 2021 provided evidence of continued progress in reducing contaminant concentrations in Site 300 groundwater and soil vapor, controlling and cleaning up contaminant sources, and

mitigating risk to on-site workers. A more detailed description of remediation progress at the Site 300 OUs in 2021 is available in the *Annual 2021 Compliance Monitoring Report for LLNL Site* 300 (Buscheck et al., 2022).

7.2.4 Environmental Impacts

LLNL strives to reduce elevated risks arising from chemicals released to the environment at Site 300, to conduct its activities to protect ecological resources, and to protect the health and safety of site workers. LLNL's cleanup remedies at Site 300 are designed and implemented to achieve the goals of reducing risks to human health and the environment and satisfying remediation action objectives, meeting cleanup standards for chemicals and radionuclides in water and soil, and preventing contaminant migration in groundwater to the extent technically and economically feasible.

These actions include:

- Groundwater and soil vapor extraction and treatment.
- Source control through the capping of lagoons and landfills, removal and remediation of contaminated soil, and hydraulic drainage diversion.
- Monitoring natural attenuation.
- Monitoring and institutional controls.

These remedies are selected by DOE and the regulatory agencies with public input.